[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF CORNING GLASS WORKS AND DOW CORNING CORPORATION]

Sodium and Potassium Salts of Triorganosilanols

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Sodium salts of dimethylphenyl-, methyldiphenyl- and triphenylsilanols have been prepared in high yields by the action of sodium hydroxide on the corresponding disiloxanes in alcohol solutions. These salts are readily converted to the silanols by mild hydrolysis. Anhydrous trimethylsilanol sodium salt has been prepared in low yield by this process and in higher yields from reactions of sodium oxide or sodamide on the disiloxane. Trimethylsilanol potassium salt has been obtained from hexamethyldisiloxane by prolonged reflux with the hydroxide and in high yield from the reaction with the amide. The new anhydrous salts are characterized by X-ray powder diffraction data and their identities are established by condensations with appropriate chlorosilanes to form previously reported methylphenyldisiloxanes. Application of this analog of the Williamson synthesis to these salts has also afforded the following new methylphenylsiloxanes: $Ph_2Si(OSiPhMe_2)_2$, $PhSi(OSiPhMe_2)_3$ and $Me_3Si[OSiPhMe]_3OSiMe_3$.

Since early work by Friedel and Ladenburg[1,2] there has been an interest in the alkali metal salts of silanols and siloxanols which are akin to inorganic silicates, except that they have organic groups attached to silicon by C–Si bonds. Both mono-organo[1,3,4a–c] and diorgano[4b–d,5,7b] salts have been prepared as aqueous solutions by the action of alkali on siloxanes and silanols; crystalline species were isolated in several instances.[3d–e,5c] However, until recently, triorganosilanol salts have been reported only from the action of sodium metal on the silanols[2,6,7b]; sodium salts of triethyl-,[2,6d,7b] tri-*n*-propyl-,[6a] triisoamyl-,[6b] triphenyl-[6c,7b] and trimethylsilanols[6d–e,7b] have been prepared in this manner.

In the case of the trimethylsilanol reaction with sodium, Sommer, *et al.*, found the theoretical amount of hydrogen was evolved[6d]; they did not isolate the salt but employed its solution in benzene in condensations with silicon tetrachloride, ethyltrichlorosilane and diethyldichlorosilane.[6e] They also obtained crystalline solids, which varied in composition and were only slightly soluble in organic solvents, from a reaction of the silanol with sodium hydroxide.[6d] Similar material appears to have been obtained by Tatlock and Rochow from the action of sodium hydroxide on hexamethyldisiloxane in aprotic solvents.[7a] This type of product appears to differ markedly from an anhydrous trimethylsilanol salt which we have obtained from reactions of hexamethyldisiloxane with sodium amide[8a] or hydroxide[4b,8b] and of trimethylethoxysilane with sodium hydroxide.[4b,8b] Tatlock and Rochow recently employed the reaction of trimethylsilanol with metallic sodium, potassium and lithium to prepare corresponding salts, which they isolated and characterized as crystalline species. They also used these salts for reactions with several heavy metal chlorides. Our anhydrous sodium and potassium[4b,8] salts of trimethylsilanol appear to be the same as theirs.

In this paper, the first of a series on sodium and potassium salts of silanols and siloxanols, preparation of the anhydrous sodium salts of trimethyl-, dimethylphenyl-, methyldiphenyl- and triphenylsilanols and of the potassium salt of trimethylsilanol from the corresponding disiloxanes and alkali metal hydroxides are described.[8] The success of

$$(R_3Si)_2O + 2NaOH \rightleftarrows 2R_3SiONa + H_2O$$

the preparation depends upon a complete removal of water to effect dehydration of the salt, as well as to force the equilibrium shown in the desired direction. However, this method is complicated by formation of salt hydrates, alcoholates and double salts with the alkali metal hydroxides. It is generally accomplished most advantageously, with stoichiometric amounts of the reagents being brought into a single phase, by (1) dissolving, with heating, in methanol or methanol–isopropyl alcohol mixtures, (2) refluxing several hours with a gradual removal of solvent until solids separate or until the residue becomes viscous (but not above 150°), (3) retreating with alcohol several times, with concentration following each treatment, until dehydration is essentially complete, and (4) heating below 150° in vacuum to expel residual solvent. The temperature during the concentrations is held below 150° to minimize possible hydrolytic cleavage of the organic groups. In the case of the methyldiphenyl and triphenyl compounds, addition of toluene to the alcohol solution, or in portions alternating with the alcohol, was employed to enhance solubility and to facilitate dehydration on distillation. Some of the crystalline solids, which separate at intermediate stages, have been found to be salt

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[1] C. Friedel and and A. Ladenburg, *Ber.*, **3**, 15 (1870); *Ann.*, **159**, 259 (1871); A. Ladenburg, *Ber.*, **6**, 379, 1029 (1873); *Ann.*, **164**, 309 (1872); **173**, 143 (1874).

[2] A. Ladenburg, *Ber.*, **4**, 901 (1871); *Ann.*, **164**, 320 (1872).

[3] (a) E. Khotinsky and B. Seregenkoff, *Ber.*, **41**, 2946 (1908); (b) W. Melzer, *ibid.*, **41**, 3390 (1908); (c) F. S. Kipping and J. E. Hackford, *J. Chem. Soc.*, **99**, 138 (1911); (d) J. A. Meads and F. S. Kipping, *ibid.*, **105**, 679 (1914); **107**, 459 (1915); (e) A. Stock and C. Somieski, *Ber.*, **52**, 695 (1919); (f) J. R. Elliot and R. H. Krieble, U. S. Patent 2,507,200 (1950); (g) C. W. MacMullen, U. S. Patent 2,587,636 (1952).

[4] (a) J. F. Hyde and O. K. Johannson, U. S. Patent 2,438,055 (1948); (b) J. F. Hyde, U. S. Patent 2,567,110 (1951); (c) J. F. Hyde, U. S. Patent 2,574,265 (1951); (d) J. F. Hyde, THIS JOURNAL, **75**, 2166 (1953).

[5] (a) G. Martin, *Ber.*, **45**, 403 (1912); (b) F. S. Kipping, *J. Chem. Soc.*, **101**, 2108, 2125 (1912); (c) R. Robinson and F. S. Kipping, *ibid.*, **101**, 2142, 2156 (1912); **105**, 2830 (1923); (d) H. S. Pink and F. S. Kipping, *ibid.*, **123**, 2830 (1923); (e) N. W. Cusa and F. S. Kipping, *ibid.*, **135**, 2205 (1932).

[6] (a) C. Pape, *Ann.*, **222**, 368 (1884); (b) F. Taurke, *Ber.*, **38**, 1666 (1905); (c) W. Schlenk, J. Renning and G. Racky, *ibid.*, **44**, 1178 (1911); (d) L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, THIS JOURNAL, **68**, 2282 (1946); (e) L. H. Sommer, L. Q. Green and F. C. Whitmore, *ibid.*, **71**, 3253 (1949).

[7] (a) W. S. Tatlock and E. G. Rochow, *ibid.*, **72**, 528 (1950); (b) *J. Org. Chem.*, **17**, 1555 (1952).

[8] J. F. Hyde and O. K. Johansson, U. S. Patents (a) 2,453,092, (b) 2,472,799 (1949).

hydrates; others were found to be poorly soluble and alkali-rich addition compounds or mixtures. Such intermediate products from a large number of preparations have been found to vary considerably in composition; as obtained from solution they possess neutral equivalents which are both higher and lower than the values calculated for the anhydrous salts. However, most of these products redissolve when retreated with alcohols and are then further dehydrated. The simple anhydrous salts having phenyl groups were obtained finally in essentially quantitative yields.

The sodium and potassium salts of trimethylsilanol were obtained with more difficulty and in lower yield than the phenyl-containing salts by the disiloxane–hydroxide reaction. The products obtained in these cases were principally complexes, containing the hydroxide and water, which were difficult to convert to the normal salt; the process was further complicated by the comparatively low boiling points of hexamethyldisiloxane and the probable intermediate trimethylsilanol. Furthermore, trimethylsilanol is thought to be a weaker acid than the phenyl-containing silanols and, consequently, it does not compete as effectively with the water and alcohol in its acceptance of the base. However, some of the soluble normal anhydrous salt was isolated from the sodium-rich products by petroleum ether extraction. The insoluble residue from the extraction is thought to be principally the complex $Me_3SiONa{\cdot}NaOH$. The potassium salt was not obtained by this process, but by prolonged refluxing of an excess of the disiloxane, in which the hydroxide was held in suspension. The hydroxide was gradually replaced by new crystalline phases; a hydrated salt was isolated by ether extraction and dehydrated by heating *in vacuo*. The anhydrous potassium salt may be recrystallized from diethyl ether. Both the anhydrous sodium and potassium salts may be sublimed below 150° under high vacuum.

Another procedure used for preparing the trimethylsilanol sodium salt consisted in employing commercial sodium oxide in place of the hydroxide so as to obviate most of the dehydration difficulties; the oxide reacted with the disiloxane, in excess, and in a pyridine–methanol solution, during a long reflux period. Although some of the alkali-rich material was still obtained, the anhydrous salt formed in higher yields than in the hydroxide reaction.

The most satisfactory method which we have found for preparing both the sodium and potassium salts of trimethylsilanol is by the amide reaction.[8a]

$$2(Me_3Si)_2O + 2NaNH_2 \longrightarrow 2\ Me_3SiONa + (Me_3Si)_2NH + NH_3$$

In this strictly anhydrous system, formation of the troublesome complexes with water and sodium hydroxide is obviated. The reaction may be carried out in the liquid ammonia solution in which the amide is prepared, or in ether in which the amide is suspended, and to which the disiloxane is cautiously added. Based on the amide, essentially quantitative yields of the anhydrous salts are obtained. The silazane formed is volatile and readily removed.

The formation of the salts from alkali in the presence of methanol and isopropyl alcohol shows that silanols have an acidic character somewhat greater than alcohols. This constitutes further evidence of a polarizing effect due to the more positive character of the silicon atom compared to carbon.[4d,9]

The various triorganosilanol salts are strongly alkaline. They have solubilities in organic solvents, including petroleum ether and benzene, which are quite high for alkali salts; thus suitable solvents for recrystallization may be selected. Since they are very hygroscopic, they must be protected from moisture in storage. Under suitable conditions hydrates form, but exposure to excess moisture results in their hydrolysis to corresponding silanols and disiloxanes. Trimethylsilanol is immediately noticeable by its odor, when its salts are exposed to moisture.

Most of the anhydrous salts sublimed or decomposed without melting and were therefore characterized by X-ray powder diffraction data. Their identities were established by (1) their neutral equivalents, (2) high conversions to corresponding silanols by mild hydrolysis in ether with dilute acetic acid, and (3) reaction with appropriate chlorosilanes to form known unsymmetrical methylphenyldisiloxanes[10] in high yields. These condensations and others of this type[4b,6e] have proved to be most useful in synthesizing some specific siloxanes in higher yields than are obtained by methods involving co-hydrolysis or siloxane rearrangement.[10] This method was employed with the trimethyl- and dimethylphenylsilanol salts for the synthesis of several new methylphenylsiloxanes which are of interest as heat exchange media and diffusion pump fluids.[10,11] These compositions include the trisiloxane $Ph_2Si(OSiPhMe_2)_2$, the tetrasiloxane, $PhSi(OSiPhMe_2)_3$, and the pentasiloxane (diastereomeric mixture) $Me_3Si[OSiPhMe]_3OSiMe_3$.

Experimental

Trimethylsilanol Sodium Salt. A. From Sodium Amide.—The amide was prepared from a solution of 4.2 g. of sodium metal in 100 ml. of liquid ammonia, at about −33° with 0.1 g. of ferric nitrate as catalyst.[12] The solution of the amide was vigorously stirred with a stream of gaseous ammonia while 45.9 g. of hexamethyldisiloxane was added dropwise. The ammonia was allowed to evaporate, leaving a mass of large crystals partially covered with liquid. These were dissolved in ether, and the solution was filtered under nitrogen through a fritted glass funnel. Volatiles were removed under reduced pressure, with final heating of the solid residue to 100°. On fractionating the volatile materials, 18.4 g. of hexamethyldisilazane was obtained. The residue consisted of finely divided crystals of the silanol salt; yield 17.0 g. (80%).

Anal. Calcd. for C_3H_9SiONa: neut. equiv., 112.2. Found: neut. equiv., 112.5, 113.0.

Trimethylsilanol sodium salt is extremely soluble in diethyl ether and benzene and moderately soluble in petroleum ether. It can be sublimed under high vacuum at 130–140°.

B. From Sodium Hydroxide (and Oxide).—When 6.2 g. of sodium oxide was heated in a solution of 16.2 g. of hexamethyldisiloxane and 20 to 25 ml. of methanol, it dissolved.

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(9) H. Gilman and G. E. Dunn, *Chem. Revs.*, **52**, 77 (1953).

(10) W. H. Daudt and J. F. Hyde, THIS JOURNAL, **74**, 386 (1952).

(11) M. J. Hunter, U. S. Patent 2,530,356 (1950).

(12) T. H. Vaughn, R. R. Vogt and J. A. Nieuwland, THIS JOURNAL, **56**, 2120 (1934).

X-RAY POWDER PATTERN DATA[a]

d, kX.	2.42	1.71
I/I_0	1.00	0.35

[a] Patterns were obtained with a small Philips Diffraction Unit using filtered CuKα radiation; d is interplanar spacing, I/I_0 is relative intensity.

However, upon distillation 14.4 g. of the disiloxane was recovered. The disiloxane was returned to the oxide residue, and 1.8 g. of water and 20 ml. of methanol was added to form a hydroxide solution. The mixture was then refluxed for 1 to 2 hours. Upon cooling it crystallized in the form of long needles.

After vacuum drying at 25° there was obtained 34 g. of an alcohol salt complex; neut. equiv. 176.5. Extraction with 50 to 75 ml. of refluxing 90–100% petroleum ether left 8.5 g. of insoluble crystals, neut. equiv. 79.5. Further reflux of the solution caused the precipitation of another 1 to 2 g. of crystals, neut. equiv., 132.5. The filtrate became very viscous as it was concentrated and with complete solvent removal it finally crystallized; yield 27%, neut. equiv. 114.5.

In another preparation, a mixture of 32.4 g. of hexamethyldisiloxane, 12.4 g. of sodium oxide, 25 ml. of pyridine and 3 ml. of methanol was warmed with stirring for 6 days. The sodium oxide had largely dissolved and a fine precipitate had collected on the walls of the flask. This was extracted with petroleum ether and the filtrate was evaporated to dryness, yielding 22 g. (49%) of the desired salt as shown by its neutral equivalent and X-ray diffraction pattern.

A 22.6-g. (0.2 mole) sample of the salt was dissolved in 200 ml. of benzene and added in 10 minutes, with stirring, to 59 g. of triphenylchlorosilane in 200 ml. of benzene at 50–60°. The mixture was clear but became cloudy in an hour; it tested slightly alkaline for the most part, but it contained both acidic and basic solid specks. It was made faintly acid by adding 1.5 ml. of trimethylchlorosilane; 200 ml. of ether was added and stirring was continued overnight at 30–50° to coagulate the salt to a fine precipitate. The solution was washed with water and filtered from a 4.7 g. crop of undissolved hexaphenyldisiloxane, m.p. 226–228°. The filtrate was then strip-distilled to remove solvent, followed by 60.0 g. (86%) of **1,1,1-trimethyltriphenyldisiloxane**,[10] b.p. 140–145°, m.p. 46–49° after crystallization on standing overnight. Recrystallization from 100 ml. of isopropyl alcohol afforded 39.4 g. of prisms, m.p. 50–51°, and trituration of the concentrated filtrate with methanol afforded 7.1 g. of a second crop of the crystals, m.p. 47–48.5°. A 2.4-g. residue from the distillation gave, with benzene–ethanol, an additional 1.0 g. (total 11%) of hexaphenyldisiloxane, m.p. 222–225°.

The salt was further characterized by condensation with silicon tetrachloride and with methyl-, ethyl- and phenyltrichlorosilanes to form the known branched siloxanes[4b,6e] $Si(OSiMe_3)_4$, $MeSi(OSiMe_3)_3$, $EtSi(OMe_3)_3$ and $PhSi(OSiMe)_3$.

Trimethylsilanol Potassium Salt. A. From Potassium Amide.—The amide was prepared from a solution of 9.9 g. of potassium in liquid ammonia with ferric oxide catalyst. The ammonia was allowed to evaporate and to the amide suspended in 100 ml. of dry diethyl ether 41 g. of hexamethyldisiloxane was added dropwise. As the reaction proceeded the amide dissolved with the liberation of sufficient heat to bring the solution to reflux. The mixture was filtered from sludge, and the filtrate was taken to dryness by evaporation under reduced pressure with final heating to 120°; yield of salt 79%.

Anal. Calcd. for C_3H_9SiOK: neut. equiv., 128.3. Found: neut. equiv. of crude product, 129.5.

Trimethylsilanol potassium salt is much less soluble in common organic solvents than the corresponding sodium salt.

X-RAY POWDER PATTERN DATA

d, kX.	9.0	4.45	3.03	2.98	2.81
I/I_0	0.68	0.92	0.76	0.56	1.00

B. From Potassium Hydroxide.—A suspension of 10.6 g. of potassium hydroxide (neut. equiv. 61.6) in 28.0 g. of hexamethyldisiloxane, was heated 10 days at 100°. The olids were extracted with diethyl ether to yield 14.2 g. of a soluble fraction, neut. equiv. 150, and an insoluble fraction with a neut. equiv. of 126. The former was dehydrated at 100° (1 to 2 mm.) to a neut. equiv. of 132. An X-ray diffraction pattern of this material matched that above.

A 20.5-g. (0.157 mole) sample of the salt was suspended in 200 ml. of diethyl ether and added in 20 minutes with stirring to 36.9 g. of 1,3,5-trimethyl-1,3,5-triphenyldichlorotrisiloxane[10] in 50 ml. of diethyl ether and then heated 18 hours under reflux. After filtering from the precipitated potassium chloride, the reaction product was concentrated to 25.8 g. (58%) of crude **nonamethyl-3,5,7-triphenylpentasiloxane**, b.p. 197–201° (2.0 mm.). This product showed slight acidity; it was therefore allowed to stand 2 days over 28% aqueous ammonia, washed and redistilled, affording the pure disiloxane, b.p. 190° (2.0 mm.), viscosity 13 cstks. at 25°, n^{25}_D 1.4932, d^{25}_4 1.0115.

Anal. Calcd. for $C_{27}H_{42}Si_5O_4$: Si, 24.57; sp. refr., 0.2878. Found: Si, 24.53, 24.42; sp. refr., 0.287.

Dimethylphenylsilanol Sodium Salt.—An 8-g. sample of sodium hydroxide was dispersed in 70 ml. of isopropyl alcohol and 30 ml. of methanol by heating nearly to boiling and crushing the pellets with a glass rod. To this solution 28.6 g. of tetramethyl-1,3-diphenyldisiloxane, b.p. 161–161.5° (15 mm.), was added, keeping the reaction mixture at 40–50°. The solution was filtered while hot to remove a small amount of sodium carbonate, and concentrated to a clear viscous liquid by heating to 115°. Crystals deposited on standing which contained a much higher percentage of sodium than the desired salt. These were redissolved in the reaction mixture by addition of 5 ml. of methanol with gentle warming. The solution was again concentrated by gradually heating to 140° at 15 mm. The reaction was forced to completion finally by repeating the addition of methanol and heating under vacuum three more times. The resulting viscous product crystallized completely on standing; yield 33 g., neut. equiv. 169.5. Recrystallization from petroleum ether afforded fine needles, m.p. 87–94°.

Anal. Calcd. for $C_8H_{11}SiONa$: Si, 16.09; Na, 13.22; neut. equiv., 174.2. Found: Si, 15.79; Na, 12.66; neut. equiv., 176.6.

X-RAY POWDER PATTERN DATA

d, kX.	I/I_0	d, kX.	I/I_0	d, kX.	I/I_0
6.97	0.49	4.15	0.86	2.54	0.37
6.11	.34	3.87	1.00	2.42	.69
5.57	.80	3.62	0.31	2.21	.31
5.28	.53	3.52	.31	2.15	.29
4.42	.51	2.93	.46	2.08	.29

A 25-g. portion of dimethylphenylsilanol sodium salt in diethyl ether was hydrolyzed by slowly adding it to a cooled mixture of 12 ml. of glacial acetic acid, 150 ml. of diethyl ether and 300 ml. of water. The ether layer was washed with distilled water, dried with anhydrous sodium sulfate and concentrated. Distillation afforded 20.8 g. (95%) of **dimethylphenylsilanol**, b.p. 101–101.5° (14 mm.); n^{25}_D 1.5100, d^{25}_4 0.990.

Anal. Calcd. for $C_8H_{12}SiO$: Si, 18.40; OH, 11.2; mol. wt., 152. Found: Si, 18.77; OH, 10.94, 11.35; mol. wt. (acetic acid), 141, 174, 157.2.

To a solution of 62.2 g. of the salt in 30–60° petroleum ether, 62.2 g. of diphenyldichlorosilane was added dropwise with stirring. The mixture was refluxed for 8 hours, filtered, washed and concentrated. Distillation yielded 68 g. (78%) of the tetramethyltetraphenyltrisiloxane, b.p. 170–220° (0.1 mm.). A redistillation afforded **1,1,5,5-tetramethyl-1,3,3,5-tetraphenyltrisiloxane**; b.p. 257° (10 mm.), 399° (760 mm.), viscosity 32 cstks. (25°). n^{25}_D 1.5543, d^{25}_4 1.057.

Anal. Calcd. for $C_{28}H_{32}SiO_3O_2$: Si, 17.4; sp. refr., 0.304. Found: Si, 16.9, 17.1; sp. refr. 0.303.

A similar reaction of the salt with phenyltrichlorosilane in ethyl ether (or petroleum ether) afforded a 35% yield of **tetramethyl-1,3,5-triphenyl-3-(dimethylphenylsiloxy)-trisiloxane**, b.p. 217–225 (1 mm.), viscosity 19 cstk. (25°), d^{25}_4 1.060, n^{25}_D 1.528.

Anal. Calcd. for $C_{30}H_{38}Si_4O_3$: Si,. 20.1. Found: Si, 20.3, 20.6.

The salt also was identified by reaction with an equivalent amount of trimethylchlorosilane in ether giving as a principal product, **pentamethylphenyldisiloxane**,[10] b.p. 95–96° (15 mm.).

Methyldiphenylsilanol Sodium Salt.—To a solution of 8 g. of sodium hydroxide in 35 ml. of isopropyl alcohol and 35 ml. of methanol at 60° was added, with stirring, 41.0 g. of 1,3-dimethyltetraphenyldisiloxane, which dispersed readily. The resulting reaction mixture was partially dehydrated in solution by simultaneously adding 30 ml. of toluene portionwise and boiling off solvent, over a period of three hours, when the concentrated solution reached a temperature of 125°. The viscous residue was redispersed in about 10 ml. of methanol and again solvent was evaporated, concurrent with portionwise addition of 30 ml. of toluene, until the boiling temperature reached 130°. After a third methanol-toluene treatment with concentration to 130°, followed by cooling and addition of 5 ml. of methanol, the salt partially crystallized. The partially crystalline mass was redissolved by heating with 25 ml. of additional toluene. The warm solution was then filtered from a small amount of suspended carbonate and concentrated for a fourth time to 135°. Upon cooling the product was highly viscous, but crystallized rapidly and extensively upon seeding. This indicated that the dehydration was essentially complete. The crystals were separated and rinsed with 30–75° petroleum ether; yield 31 g. with neut. equiv. 233.5. A second crop of 5 g. of crystals was obtained upon further concentrating from the mother liquor, yielding a total of 76% of product.

Anal. Calcd. for $C_{13}H_{13}SiONa$: neut. equiv., 236.3; Si, 11.86; Na, 9.75. Found: neut. equiv., 238; Si, 10.17; Na, 9.54.

X-RAY POWDER PATTERN DATA

d, kX.	I/I_0	*d*, kX.	I/I_0	*d*, kX.	I/I_0
13.19	0.64	5.47	0.77	4.19	0.39
11.48	.62	5.10	1.00	3.93	.35
9.61	.40	5.85	0.58	3.27	.23
8.59	.67	4.72	.71	2.51	.31
8.35	.81	4.58	.83		
6.81	.31	4.46	.75		

Hydrolysis of a 5-g. sample of the salt with dilute acetic acid, using the procedure employed with the dimethylphenylsilanol salt, afforded 4.1 g. (96%) of **methyldiphenylsilanol**,[10] b.p. 165–168° (14 mm.), $n^{25}\text{D}$ 1.579.

Anal. Calcd. for $C_{13}H_{14}SiO$: Si, 13.09; OH, 7.9; mol. wt., 214. Found: Si, 13.02; OH, 7.76, 7.74; mol. wt. (acetic acid), 227.

A 4.15-g. sample of the salt was added in small portions to 5.05 g. of triphenylchlorosilane in 25 g. of benzene. Concentration of the resulting clear mixture gave a transparent sodium chloride gel. The latter was coagulated by adding 25 g. each of diethyl ether and benzene, and refluxing four hours. It was then separated by filtration. The concentrated filtrate yielded 6.4 g. (79%) of prisms of **methylpentaphenyldisiloxane**,[10] m.p. 67.5–72.5°, from ethyl acetate. Recrystallization from petroleum ether and from acetone–ethanol gave purified disiloxane as prisms, m.p. 75.2–75.8°.

The salt was further characterized by reaction in toluene with an equivalent amount of trimethylchlorosilane to form **tetramethyl-1,1-diphenyldisiloxane**,[10] b.p. 155–158° (13 mm.), $n^{25}\text{D}$ 1.519, in 83% yield.

Triphenylsilanol Sodium Salt.—To a slurry of 26.7 g. of hexaphenyldisiloxane and a solution of 4 g. of sodium hydroxide, in 20 ml. of isopropyl alcohol and 40 ml. of methanol, 30 ml. of toluene was added gradually with warming. Upon reaching 100° the disiloxane had dissolved. However, with further heating to 115°, solids began to separate; they were accordingly redissolved by adding 10 ml. of isopropyl alcohol. The solution was again concentrated until the appearance of solids, which were again dissolved as before. On the third concentration, crystallization was allowed to proceed to completion, with heating to 150° under reduced pressure. The solid product was redissolved in 40 ml. of toluene and 3 ml. of isopropyl alcohol, filtered from a trace of solids, concentrated to half its volume, and allowed to cool. The crystals, which deposited on standing, were rinsed with toluene and dried by warming *in vacuo;* yield 26 g. (81%). They carbonized without melting at 300–350° in a vacuum.

Anal. Calcd. for $C_{16}H_{15}SiONa$: neut. equiv., 298.4. Found: neut. equiv., 296.0, 298.9.

X-RAY POWDER PATTERN DATA

d, kX.	I/I_0	*d*, kX.	I/I_0
10.78	0.40	4.62	1.00
10.40	.44	4.15	0.13
9.83	.22	2.98	0.11
5.83	.19		

The salt, with neut. equiv. 303.8, was similarly prepared from triphenylsilanol. Hydrolysis of the salt with dilute acetic acid yielded 97% of the triphenylsilanol, m.p. 144.5–146.5°.

An 18-g. sample of the salt was allowed to react with 6.95 g. of trimethylchlorosilane in a toluene–ether solution to form 21.5 g. (98%) of crude **1,1,1-trimethyltriphenyldisiloxane**,[10] m.p. 48–50°, containing some higher melting material. Distillation afforded 15.2 g. of a pure fraction, b.p. 215–218° (13 mm.), m.p. 48°, $n^{25}\text{D}$ 1.560 (supercooled).

MIDLAND, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Synthesis of Fluorine-containing Organosilanes

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Fluorinated organosilanes in which the perfluoroalkyl group is separated from the silicon atom by an ethylene group have been prepared by reaction of the Grignard reagent of 3,3,4,4,5,5,5-heptafluoro-1-bromopentane and silicon tetrachloride or ethyl silicate. The bromide was prepared by dehydration of 3,3,4,4,5,5,5-heptafluoro-2-pentanol followed by addition of hydrogen bromide to the olefin in the presence of activated carbon. A silanol, silanediol and disiloxane were prepared from the fluorinated silanes as well as silicone oils.

The most convenient method for the synthesis of organosilanes is the reaction of silicon tetrachloride or ethyl silicate with a Grignard reagent. For the preparation of fluorinated organosilanes this investigation has made use of the readily available 3,3,4,4,5,5,5-heptafluoro-1-bromopentane in which the bromine atom is separated from the perfluoroalkyl group by an ethylene group which would be expected to completely mask the powerful electron attracting effect of the fluorinated portion of the carbon chain. Therefore, this bromide, as contrasted to a more fully fluorinated alkyl bromide, would be expected to form a normal Grignard reagent.

The starting material, 3,3,4,4,5,5,5-heptafluoro-2-pentanol, was prepared by reaction of ethyl heptafluorobutyrate with a mixture of methyl and isopropyl Grignard reagents.[2] The secondary alcohol

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(1) Presented before the Division of Organic Chemistry, 123rd National Meeting of the American Chemical Society, 1953.

(2) O. R. Pierce, E. T. McBee and J. C. Siegle, unpublished results.